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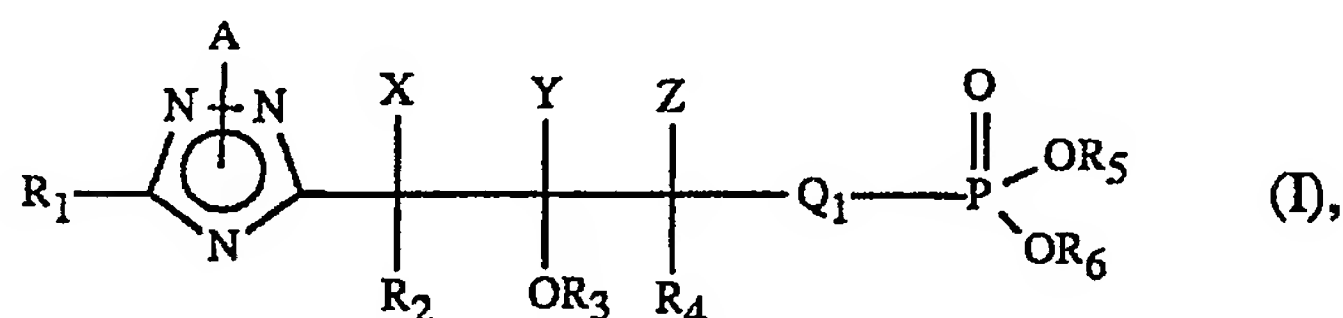
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GB 2158071 A GB 2114133 A

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(54) Triazolyl alkyl phosphates or phosphonates

(57) A Triazoles of the formula I



wherein

Q₁ is -(CH₂)_u- or -(CH₂)_u-O-, u being 0 or 1, and the other symbols are hydrogen or have various defined meanings, have a herbicidal and plant-growth regulating action. They are suitable as active substances in weed killers and in compositions for positively influencing the growth of crop plants.

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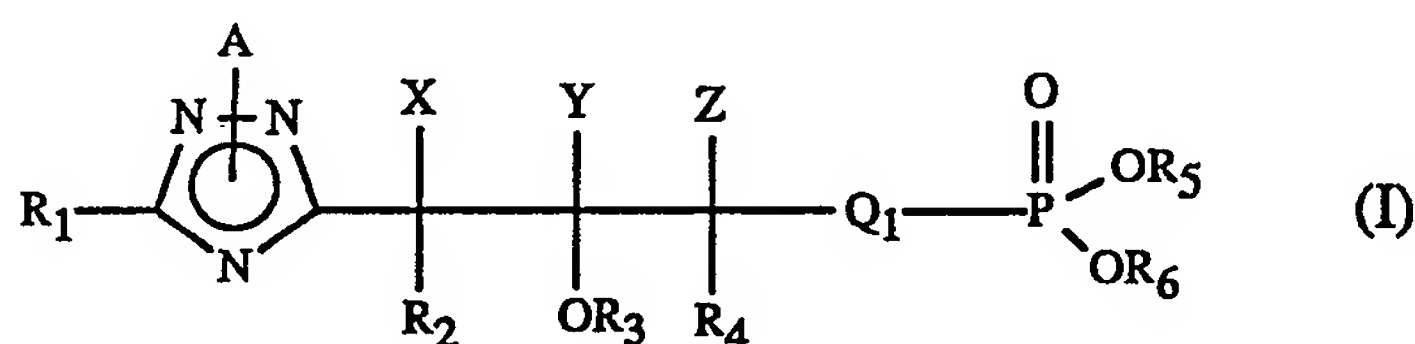
Novel Triazoles

The present invention relates to novel triazoles which have a herbicidal action and are plant-growth-regulating, to processes for their preparation, to compositions containing them as active substances, and to their use for controlling weeds, especially selectively in crops, or for regulating and inhibiting plant growth.

Triazole compounds which have a herbicidal action are generally known. For example, European Patent Application No. 0 078 613 describes herbicidally active triazole compounds.

It has been found that compounds of the formula (I) have a herbicidal and plant-growth-regulating action. They are therefore suitable as active substances in weed killers and in compositions for positively influencing the growth of crop plants.

The triazoles according to the invention are those of the formula I



in which

A is hydrogen, C₁-C₄-alkyl, triphenylmethyl, benzyl, a group $-\text{CH}_2-\text{N} \bigcirc (\text{CH}_2)_t$ or

SO₂N(CH₃)₂;

t is 4 or 5;

R₁ is hydrogen or C₁-C₄-alkyl;

X is hydrogen or C₁-C₄-alkyl;

Y is hydrogen or C₁-C₄-alkyl or together with X a -CH₂-(CH₂)_p-CH₂- group or together

with Z a $-\text{CH}_2-(\text{CH}_2)_q-\text{CH}_2-$ group;

Z is hydrogen or C_1 - C_4 -alkyl;

R_2 is hydrogen or C_1 - C_4 -alkyl;

R_3 is hydrogen, a group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Q}-\text{R}_7 \end{array}$ or a group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{R}_8 \end{array}$;

R_4 is hydrogen or C_1 - C_4 -alkyl, or together with R_2 a $-\text{CH}_2-(\text{CH}_2)_r-\text{CH}_2-$ group;

R_5 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R_6 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

Q is oxygen or sulfur;

Q_1 is $-(\text{CH}_2)_u-$ or $-(\text{CH}_2)_u-\text{O}-$;

R_7 is C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C_1 - C_4 -alkyl, halogen, halomethyl, C_1 - C_4 -alkoxy, cyano, nitro, C_1 - C_4 -alkoxycarbonyl or $\text{S}(\text{O})_m-\text{C}_1$ - C_4 -alkyl;

R_8 is C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C_1 - C_4 -alkyl, halogen, halomethyl, C_1 - C_4 -alkoxy, cyano, nitro, C_1 - C_4 -alkoxycarbonyl or $\text{S}(\text{O})_n-\text{C}_1$ - C_4 -alkyl; or is C_1 - C_6 -alkoxyalkyl, C_1 - C_6 -alkylcarbonyloxyalkyl, C_1 - C_6 -alkoxycarbonylalkyl or C_3 - C_6 -cycloalkyl;

p is 1 or 2;

q is 1 or 2;

r is 0 or 1;

m is 0, 1 or 2;

n is 0, 1 or 2; and

u is 0 or 1.

In the above definitions, halogen is to be understood as being fluorine, chlorine, bromine and iodine, preferably fluorine, chlorine and bromine.

Alkyl is, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl,

tert-butyl and the various isomeric pentyl or hexyl radicals.

Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl and 2,2,2-trichloroethyl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy; preferably methoxy.

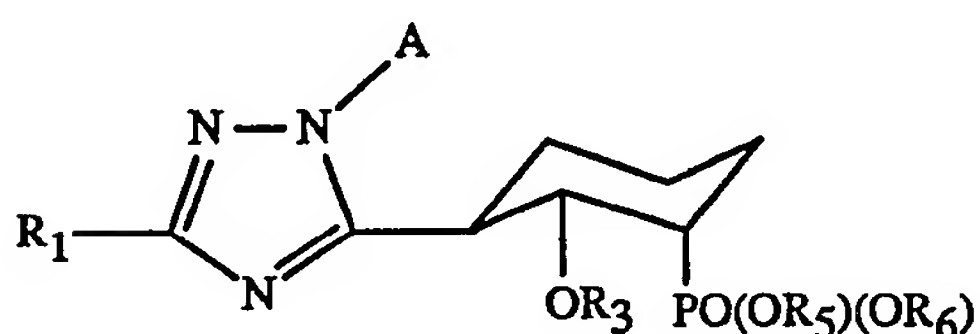
Alkenyl is to be understood as being straight-chain or branched alkenyl, for example vinyl, allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, 3-pentenyl, 2-hexenyl or 3-heptenyl. Alkenyl radicals having a chain length of 2 or 3 carbon atoms are preferred.

The alkynyl radicals occurring in the definitions of the substituents may be straight-chained or branched, for example ethynyl, propargyl, 3-butenyl, 1-methylpropargyl, 2-pentynyl or 2-hexynyl. Ethynyl and propargyl are preferred.

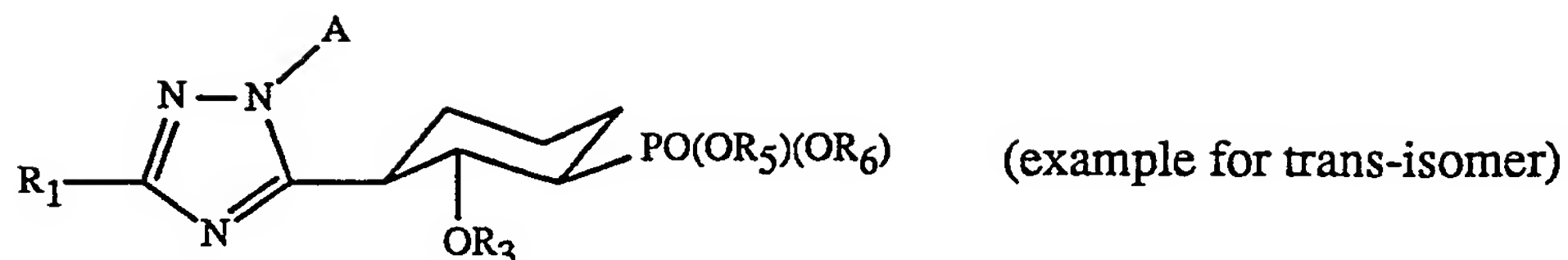
Alkoxy-carbonyl is, for example: methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl and n-butoxycarbonyl, preferably methoxycarbonyl and ethoxycarbonyl.

If the compounds of the formula I contain an asymmetric carbon atom, this results in the fact that the compounds can occur in optically isomeric forms. If there is an aliphatic C=C double bond, geometric isomerism can also occur. The formula I therefore also embraces all stereoisomers which are possible and which are in the form of enantiomers, diastereomers or their mixtures.

For compounds of the formula I, which are cyclic phosphonates, stereoisomers of the following formulae are obtained:

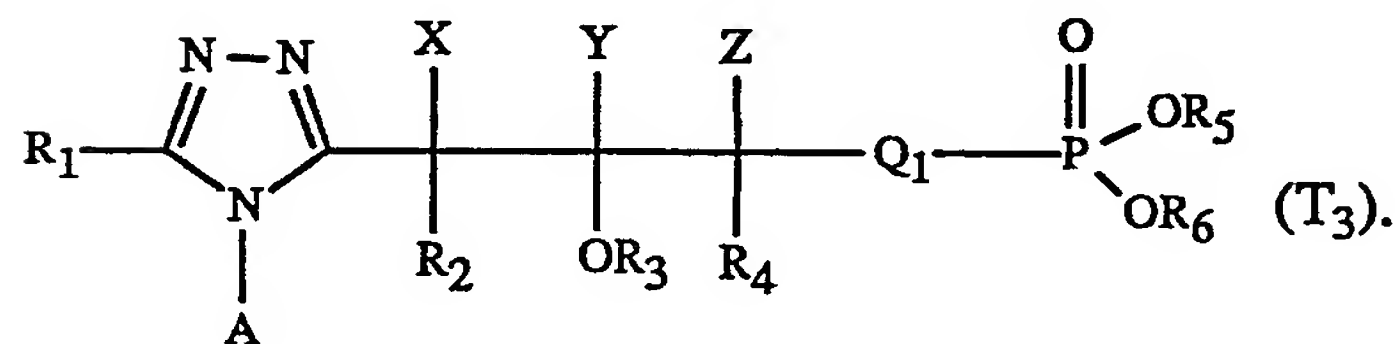
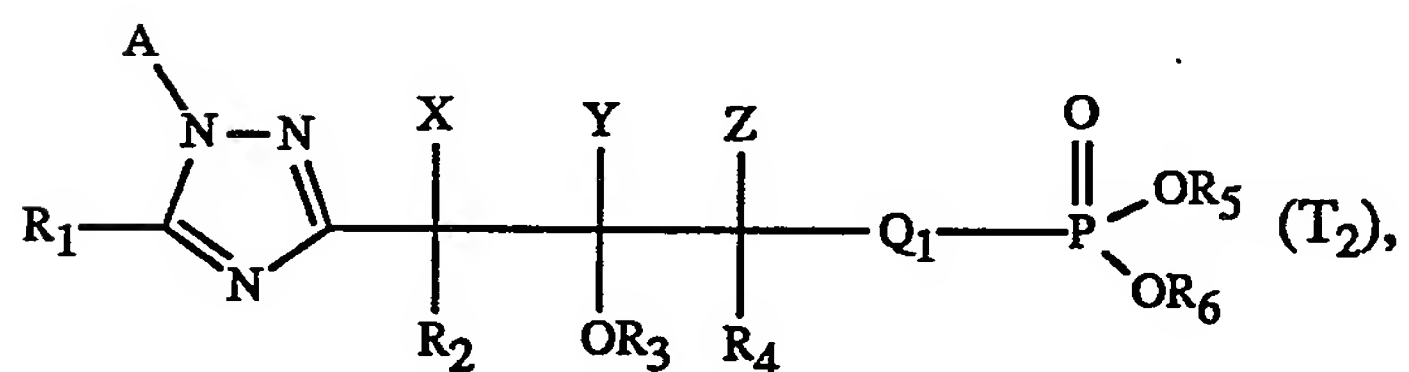
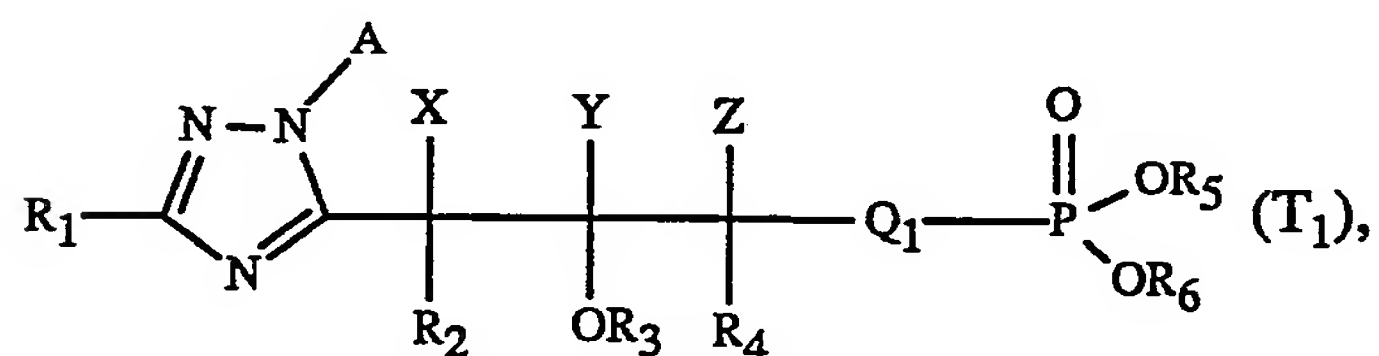


(example for cis-isomer)



The configuration of the above mentioned examples of stereoisomers of compounds of the formula I is defined according to the position of the OR₃ group and PO(OR₅)(OR₆) group.

The compounds of the formula I according to the present invention include all of the tautomeric isomers represented by the following formulae T₁, T₂ and T₃:



The term organic ammonium cation is intended to include ammonium cations prepared

from low molecular weight amines, that is to say those having a molecular weight below about 300. Examples of such amines include alkylamines, alkenylamines, and alkanolamines containing not more than two amino groups, such as methylamine, ethylamine, n-propylamine, iso-propylamine, the four isomeric butylamines, n-amylamine, iso-amylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methyl-hexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octadecylamine, ethyl-butylamine, ethyl-heptylamine, ethyl-octylamine, hexyl-heptylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, di-iso-propylamine, di-n-butylamine, di-n-amylamine, di-iso-amylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, iso-propanolamine, N,N-diethylethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine, propylendiamine, diethanolamine, tri-iso-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-sec.-butylamine, tri-n-amylamine, trimethylamine, triethylamine, tripropylamine; heterocyclic amines as, for example, pyridine, chinoline, iso-chinoline, morpholine, piperidine, pyrrolidine, indoline, chinuclidine and azepine; primary arylamines as, for example, aniline, methoxyaniline, ethoxyaniline, o,m,p-toluidine, phenylendiamine, benzidine, naphthylamine and o,m,p-chloroaniline; in particular ethyl-, propyl-, diethyl- oder triethylamine, preferably iso-propylamine and diethanolamine.

Tetra-substituted ammonium cations are also included, for example tetramethylammonium, tetrabutylammonium, benzyltrimethylammonium, benzyltriethylammonium, tetra-ethylammonium and trimethylethylammonium cations.

Trialkylsulfonium cations include those, for example, in which each of the three alkyl groups, which are not necessary all the same, may contain from 1 to 6 carbon atoms. Trialkylsulfoxonium cations likewise include those in which each of the three alkyl groups, which may be the same or different, may contain from 1 to 6 carbon atoms.

Phosphonium cations include, for example, cations in which the phosphorus atom bears four substituents, each of which may be an alkyl group of one to ten carbon atoms or a phenyl group, for example, the tetramethylphosphonium, tetrabutylphosphonium, and tetraphenylphosphonium cations.

Amidinium cations include, for example, straight chain amidinium cations of formula $R_9-C(NH_2)=NH_2^+$, wherein R_9 is an alkyl radical of, for example, from 1 to 10 carbon atoms, and cyclic amidinium cations such as 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU).

Alkali metal cations include lithium, sodium and potassium; and alkaline earth metal cations include magnesium, calcium, strontium and barium.

Preferred compounds of the formula I are those, in which

A is hydrogen, R_5 is hydrogen, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and R_6 is hydrogen, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

Preferred compounds from this group are those in which R_1 and/or R_3 is hydrogen.

Further preferred compounds of the formula I are those in which

R_1 is hydrogen; A is C_1 - C_4 -alkyl;

R_5 is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R_6 is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

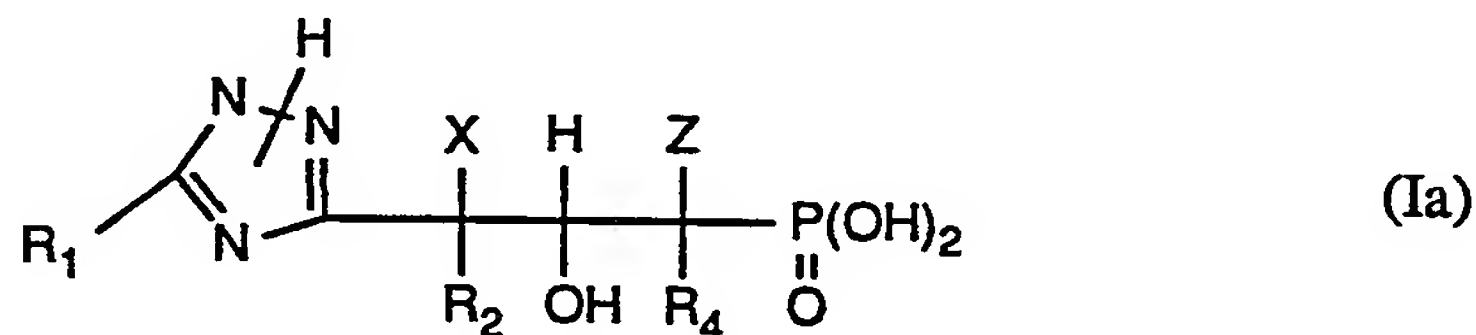
Further preferred compounds of the formula I are those in which

Q_1 is $-(CH_2)_u$, wherein u is 0.

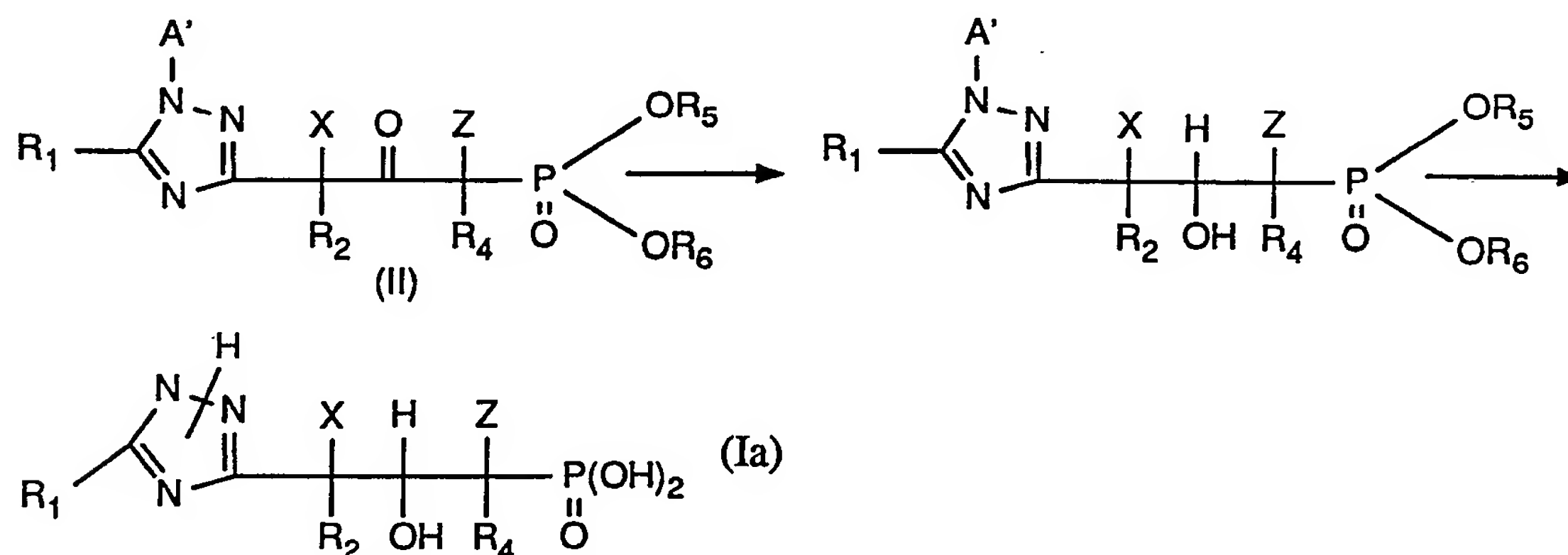
Preferred compounds of the formula I which must be emphasised are those in which R, A, R_2 , R_3 , R_4 , R_5 , R_6 , X and Z each is hydrogen.

A further subject of the present invention is a process for the preparation of compounds of the formula I which comprises

for the preparation of compounds of the formula Ia



in which R_1 , R_2 , R_4 , X and Z have the meanings given in formula I, reduction of β -ketophosphonates of the formula II with e.g. NaBH_4 in ethanol followed by hydrolysis of the phosphonate with an acid or a halosilane, or hydrogenolysis and cleavage of the protecting group A' which is triphenylmethyl, benzyl, a group $-\text{CH}_2-\text{N}(\text{CH}_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl:



β -Ketophosphonates can be prepared for example from alkyn-ols via allenic phosphonates in a manner or analogously as given by Altenbach, H.J. Tetrahedron Lett. 1981, 22, 5175.

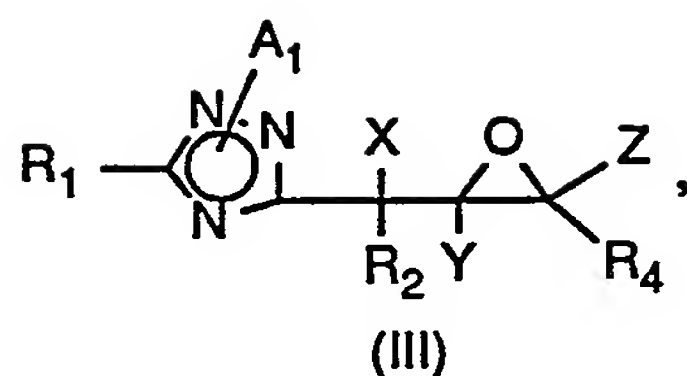
The protecting group A' as triphenylmethyl, benzyl, a group $\text{CH}_2\text{-N}(\text{CH}_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl can be cleaved by:

- hydrogenolysis or under acidic or reductive conditions for the triphenylmethyl group
- hydrogenolysis with palladium or active charcoal or by reductive cleavage by sodium in liquid ammonia for the benzyl group
- cleavage with NaBH_4 for the group $\text{CH}_2\text{-N}(\text{CH}_2)_t$
- cleavage with sodium hydroxide, sodium cyanide, tetra-*n*-butylammonium fluoride, H_2SO_4 or LiAlH_4 for the dimethylsulphamoyl group.

Said reactions are carried out in a manner or analogously as given by D.K. Anderson J. Heterocyclic Chemistry 23 (1986) p. 1257; A.R. Katritzky, Tetrahedron 46 (1990), p. 641; A.J. Carpenter, Tetrahedron 1986, 42, 2351; P.J. Dudfield Synlett. 1990, 277.

Compounds of formula I, wherein R_3 is hydrogen, can be prepared by ring-opening of

epoxides of formula III



wherein

R_1 , R_2 , R_4 , X and Z have the meanings given in formula I and A_1 is C_1 - C_4 -alkyl,

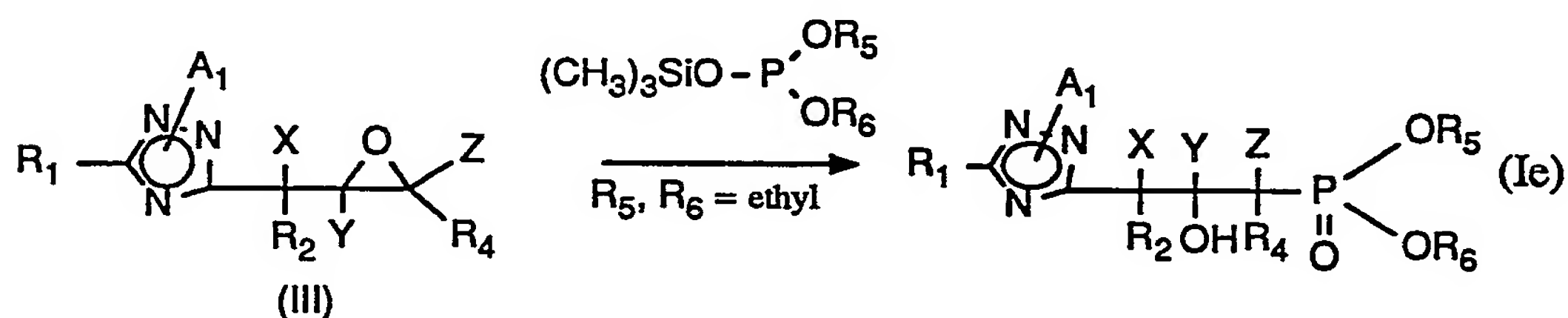
triphenylmethyl, benzyl, a group $-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or

dimethylsulphamoyl, by dialkyl phosphites or dialkyl(trialkylsilyl)phosphites catalyzed by Lewis acids or a base and optionally cleaving the protecting group A_1 .

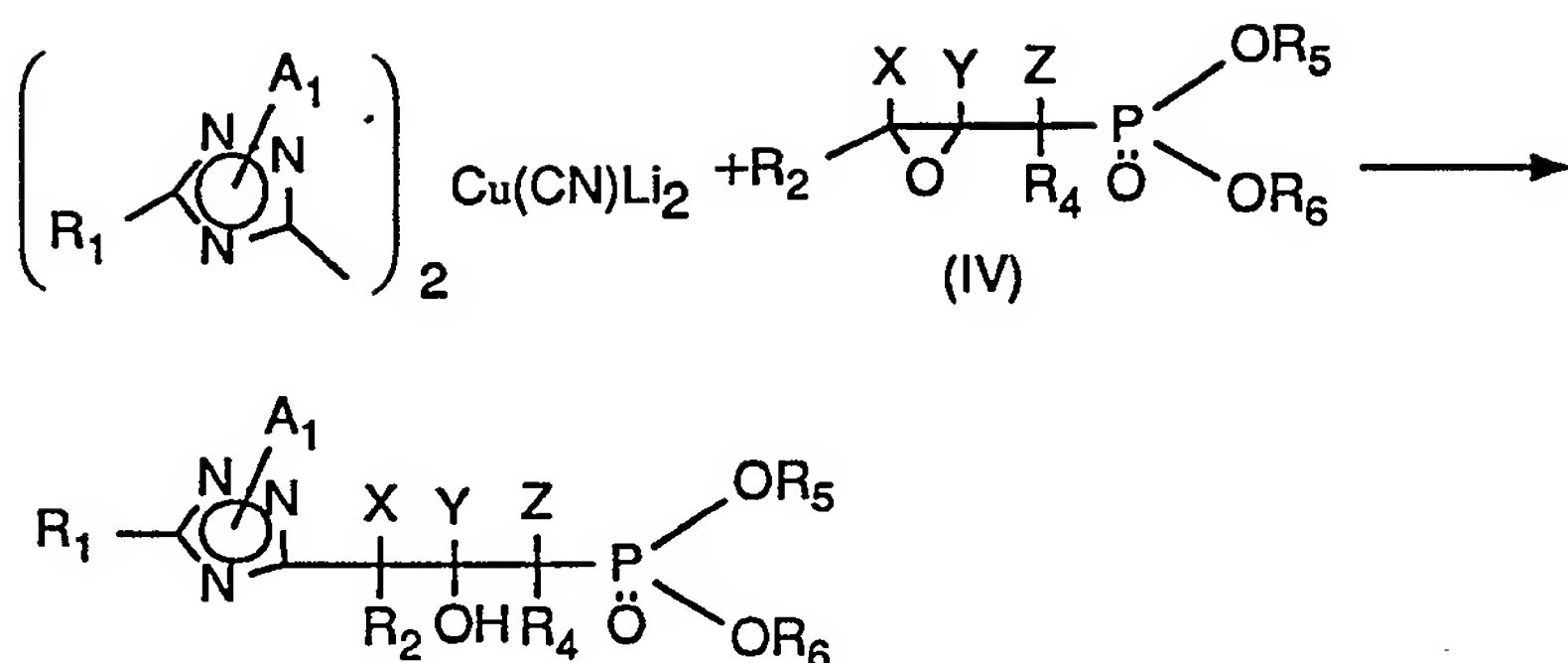
For example, compounds of formula Ie, can be prepared according to the following reaction scheme by ring-opening of epoxides of the formula III, wherein R_1 , R_2 , R_4 , Y and Z have the meanings given for formula I and A_1 is C_1 - C_4 -alkyl, triphenylmethyl, benzyl, a

group $-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl, by dialkyl

phosphites or dialkyl(trialkylsilyl)phosphites such as diethyltrimethylsilylphosphite catalyzed by Lewis acids such as zinc iodide or zinc chloride or a base such as $BF_3 \cdot OEt_2$ or $n-C_4H_9Li$ as described in Okamata, 4. Synthesis 1983, 916, and optionally cleaving the protecting group A_1 :



Alternatively, compounds of formula (I) wherein $R_3 = H$ can be prepared by cuprate induced epoxide opening in the presence of $BF_3 \cdot O(C_2H_5)_2$:



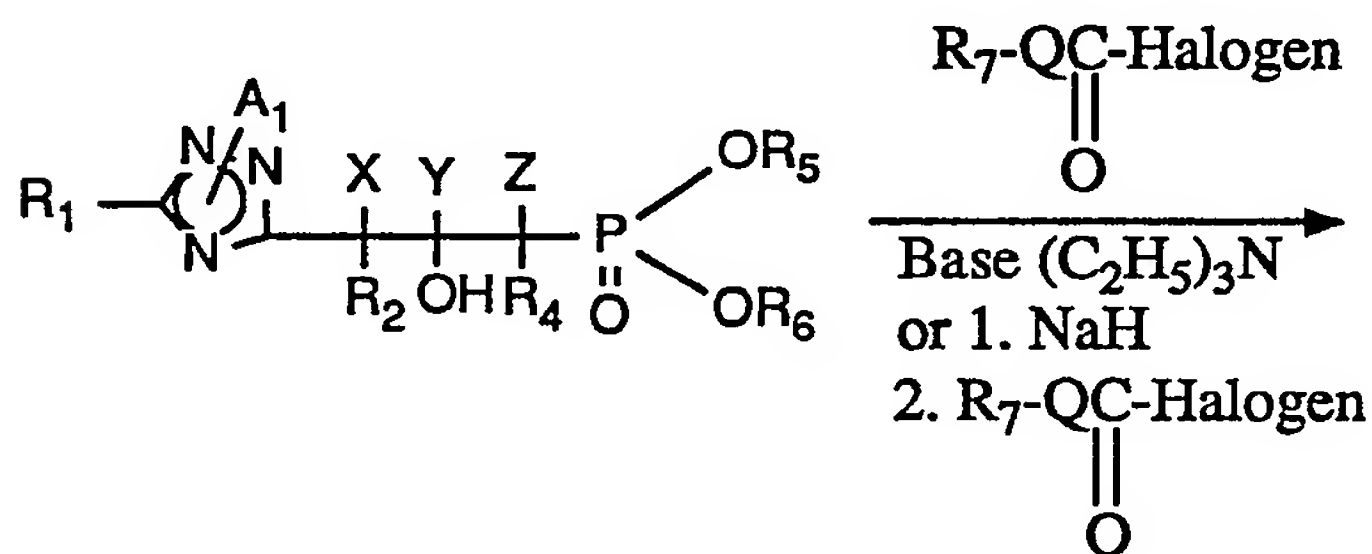
Said reactions are carried out in a manner or analogously as given by B.H. Lipschutz Org. Synth. 69, 80; B.H. Lipschutz Tetrahedron Lett. 1988, 29, 3045. The protecting group A₁ may be cleaved by methods mentioned above.

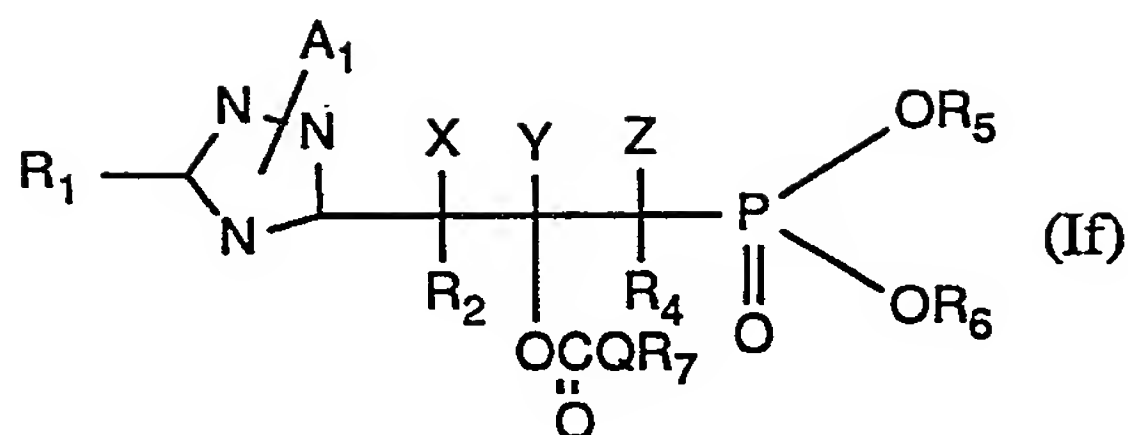
Compounds of formula I, wherein R₃ is a group $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{Q}-\text{R}_7 \end{array}$, can be prepared by

reacting a compound of formula I, wherein R₃ is hydrogen and A is A₁ mentioned above, or its sodium salt with $\begin{array}{c} \text{O} \\ || \\ \text{R}_7-\text{QC}-\text{Halogen} \end{array}$, wherein R₇ has the meaning given in formula I,

and optionally cleaving the protecting group group A₁, for example, compounds of the formula If, are prepared by reacting a compound of formula I, wherein R₃ is hydrogen and A is A₁ mentioned above, with $\begin{array}{c} \text{O} \\ || \\ \text{R}_7-\text{QC}-\text{Halogen} \end{array}$ (especially chlorine) in the presence of a

base such as (C₂H₅)₃N or by generating the sodium salt of said compound by reaction with NaH in toluene followed by reaction with $\begin{array}{c} \text{O} \\ || \\ \text{R}_7-\text{QC}-\text{Halogen} \end{array}$:

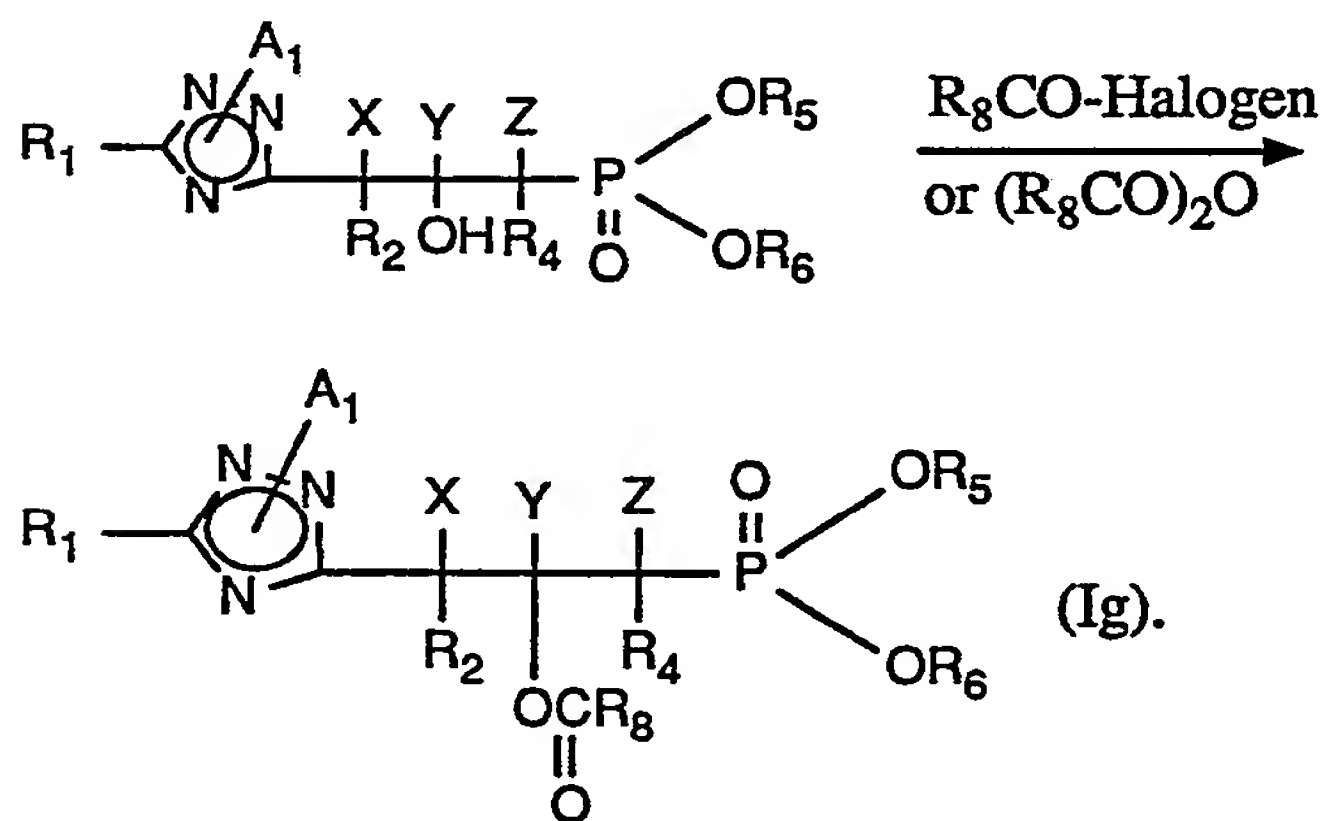




The protecting group A_1 may be cleaved by methods mentioned above.

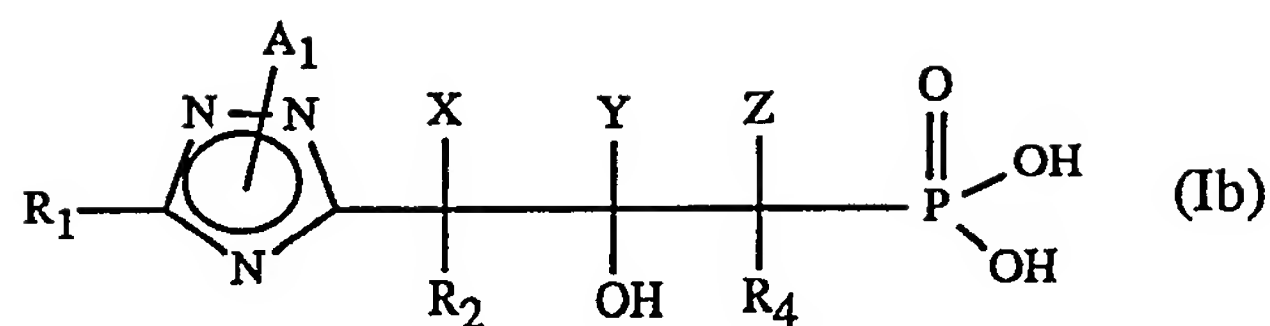
Compounds of formula I, wherein R_3 is a group CR_8 , can be prepared by reacting a

compound of formula I, wherein R_3 is hydrogen and A is A_1 mentioned above, with acid halides or anhydrides and optionally cleaving the protecting group A_1 ; for example, compounds of the formula Ig are prepared by reacting a compound of formula I, wherein R_3 is hydrogen and A is A_1 mentioned above, with acid halides or anhydrides according to the following scheme:



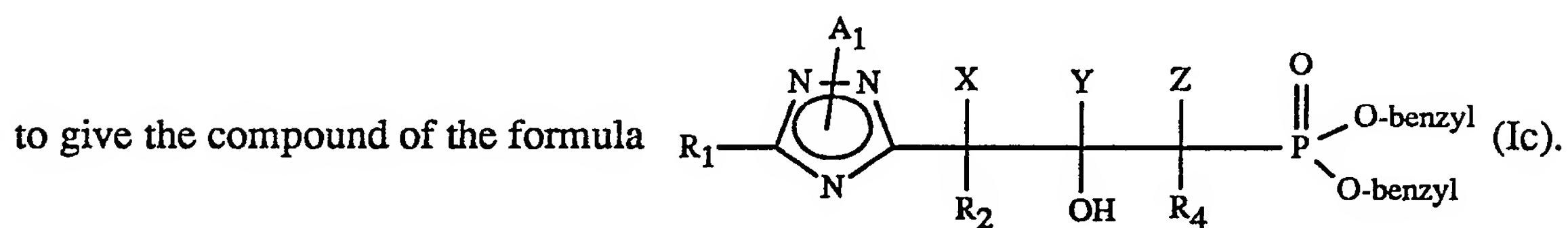
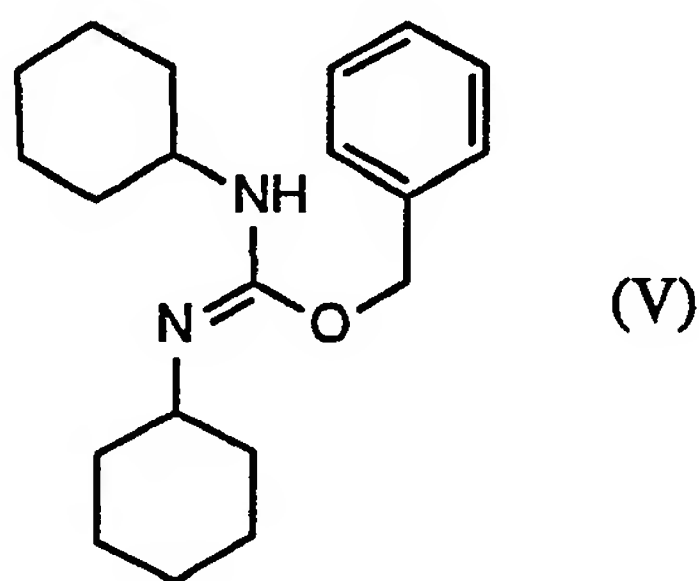
The protecting group A_1 may be cleaved by methods mentioned above. Said reaction is carried out in a manner or analogously as given in Chem. Rev. 1953. 1953, 52, p. 237-416.

Compounds of the formula I, wherein R_3 is hydrogen and R_5 and R_6 are benzyl are prepared by reacting the free phosphonic acid compound Ib



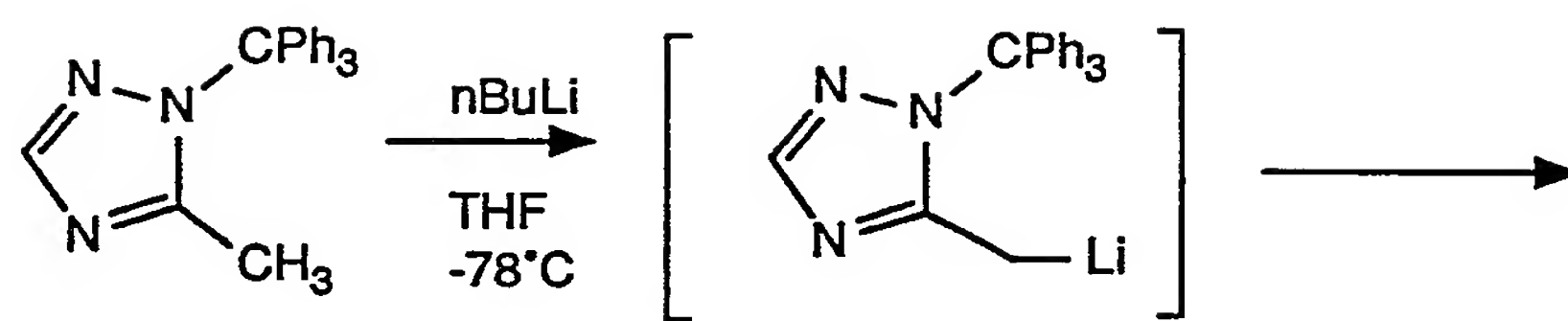
wherein R_1 , R_2 , R_4 , X , Y and Z have the meanings given under formula I and A_1 is

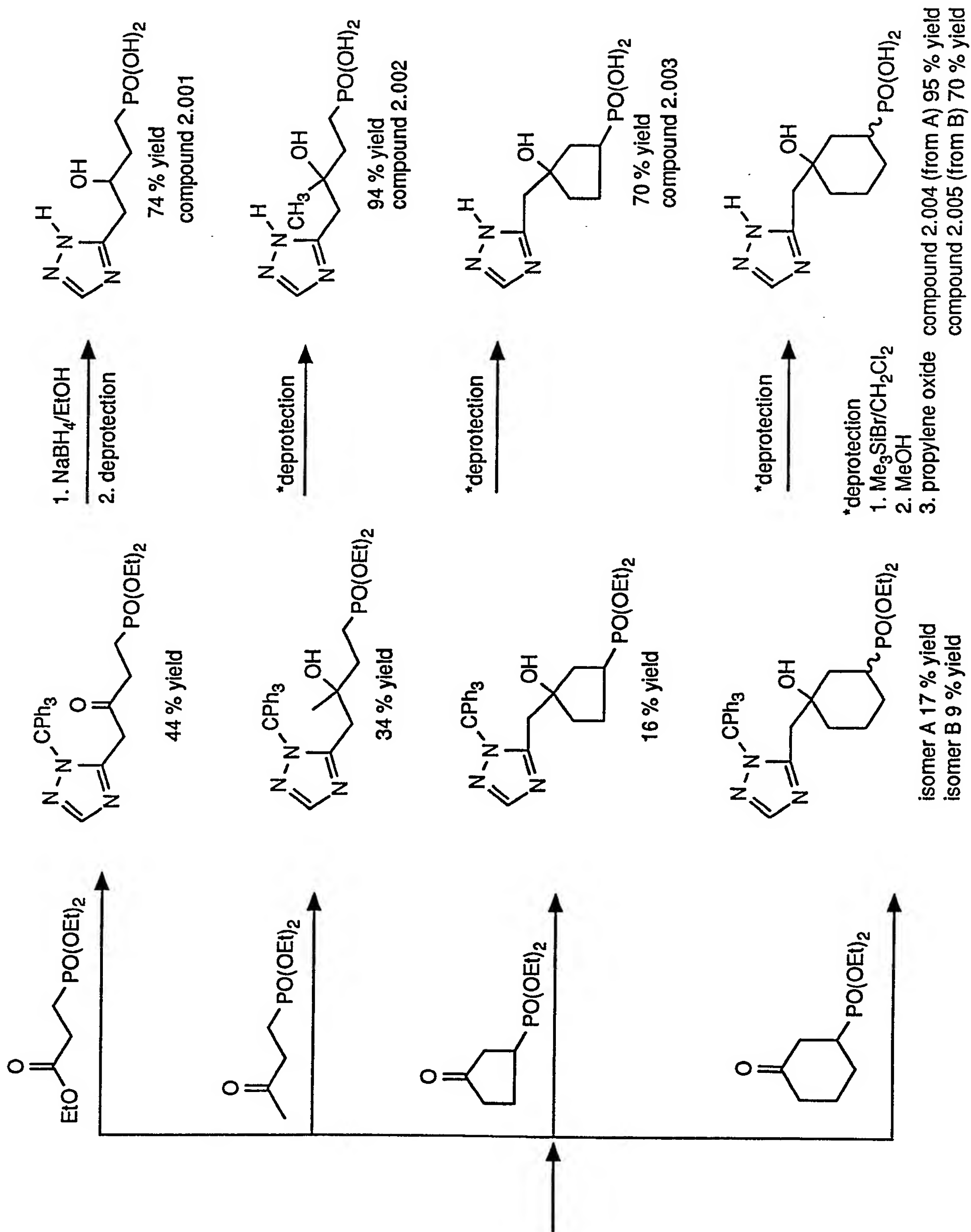
C_1 - C_4 -alkyl, triphenylmethyl, benzyl, a group $-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl; with 2 equivalents of O-benzyl-N,N'-dicyclohexylisourea of the formula



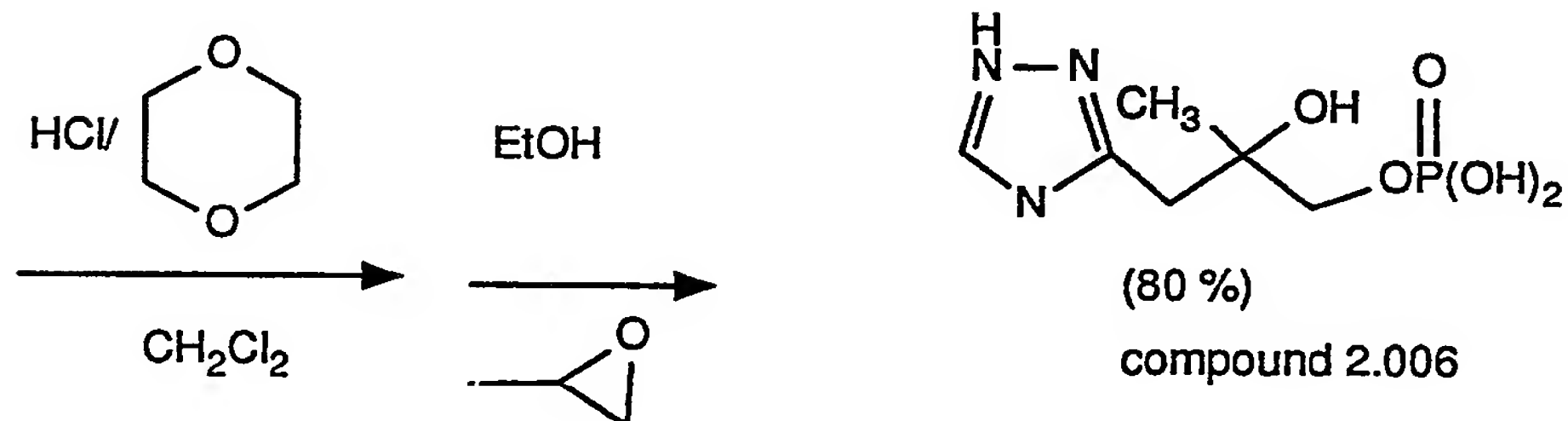
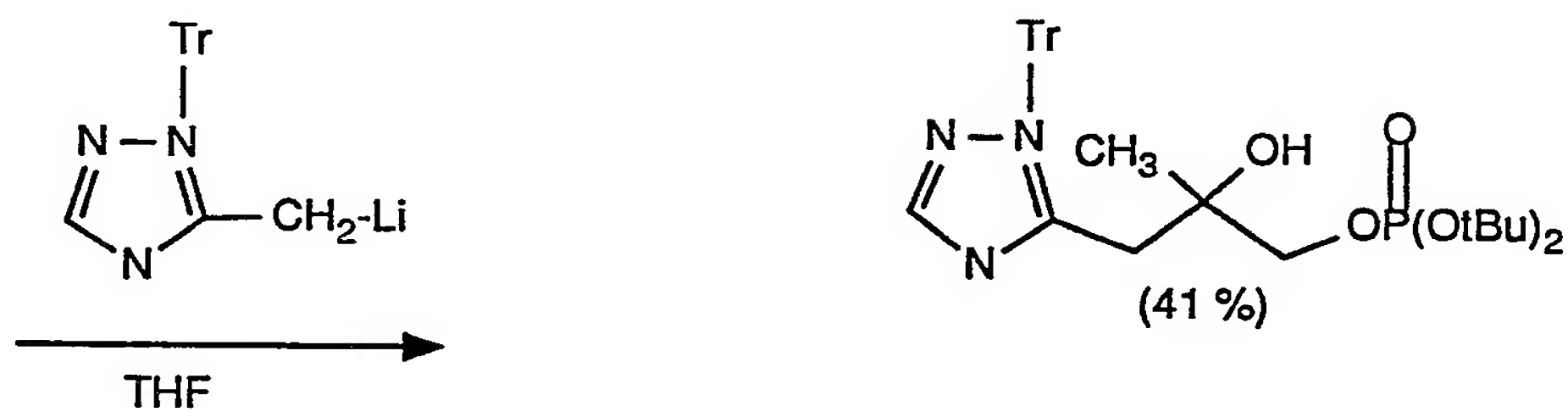
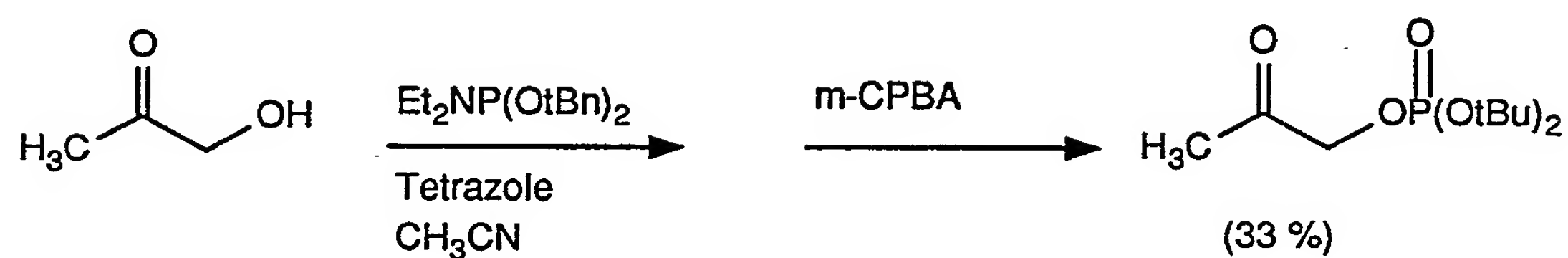
The reaction is carried out under reflux in an organic solvent such as benzene or toluene or dimethylformamide; for example in a manner or analogously as given by M. Hoffmann, Synthesis 1988, page 62 ff..

Compounds of the formula I, wherein Q_1 is $-CH_2-$ can be prepared according to the following reaction scheme:





Compounds of the formula I, wherein Q_1 is $(CH_2)_n-O-$ can be prepared according to the following reaction scheme:



The compounds of the formula I are employed in unaltered form, as obtainable by the synthesis, or preferably together with the auxiliaries conventionally used in formulation technology, and they are therefore processed in a known manner to give, for example, emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or combinations comprising the active substance of the formula I and, if desired, one or more solid or liquid additives, are prepared in a known manner, for example by intimately mixing and/or grinding the active substances with extenders, for example with solvents, solid carriers and, if desired, surface-active compounds (surfactants).

The following are possible as solvents: aromatic hydrocarbons, in particular the fractions C₈ to C₁₂, such as mixtures of alkylbenzenes, for example xylene mixtures or alkylated naphthalenes; aliphatic and cycloaliphatic hydrocarbons such as paraffins, cyclohexane or tetrahydronaphthalene; alcohols, such as ethanol, propanol or butanol; glycols as well as their ethers and esters, such as propylene glycol or dipropylene glycol ether, ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or water; vegetable oils as well as their esters, such as rapeseed oil, castor oil or soybean oil; and if appropriate also silicone oils.

Suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties, depending on the nature of the active substance of the formula I to be formulated. Surfactants are also to be understood as meaning mixtures of surfactants.

Anionic surfactants which are suitable can be either so-called water-soluble soaps or water-soluble synthetic surface-active compounds.

Suitable soaps which may be mentioned are the alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts of higher fatty acids (C₁₀-C₂₂), such as the Na salts or K salts of oleic or stearic acid, or of natural mixtures of fatty acids which can be obtained, for example, from coconut oil or tallow oil. Mention must also be made of the fatty acid methyltaurates.

However, so-called synthetic surfactants are used more frequently, in particular fatty alcohol sulfonates, fatty alcohol sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or fatty alcohol sulfates are generally in the form of alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts, and have an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals, for example the Na or Ca salt of ligninsulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and one fatty acid radical having 8 to 22 C atoms. Examples of alkylarylsulfonates are the Na, Ca or triethanolamine salts of dodecylbenzenesulfonic acid, of dibutyl-naphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensation product.

Other suitable compounds are the corresponding phosphates, such as the salts of the phosphoric ester of a p-nonylphenol/(4-14)-ethylene oxide adduct, or phospholipids.

Suitable non-ionic surfactants are mainly polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids and of alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

Other non-ionic surfactants which are suitable are the water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol which have 1 to 10 carbon atoms in the alkyl chain and which contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. The abovementioned compounds customarily contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of non-ionic surfactants which may be mentioned are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Other suitable substances are fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan trioleate.

The cationic surfactants are mainly quaternary ammonium salts, which contain at least one alkyl radical having 8 to 22 C atoms as N-substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulfates or ethylsulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customary in formulation technology are described, inter alia, in the following publications:

"McCutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, New Jersey, 1988;

M. and J. Ash. "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981.

Dr. Helmut Stache, "Tensid-Taschenbuch [Surfactant Guide]", Carl Hanser Verlag, Munich, Vienna, 1981;

As a rule, the pesticidal preparations contain 0.1 to 99 %, in particular 0.1 to 95 %, of the active substance of the formula I, 1 to 99 % of a solid or liquid additive and 0 to 25 %, in particular 0.1 to 25 %, of a surfactant.

While concentrated compositions are more preferred as commercial goods, the user generally uses dilute compositions.

The compositions can also comprise further additives such as stabilisers, for example epoxidised or unepoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), defoamers, for example silicone oil, preservatives, viscosity regulators, binders, tackifiers, as well as fertilisers or other active substances for achieving specific effects.

In particular, preferred formulations have the following composition: (% = per cent by weight)

Emulsifiable concentrates:

Active ingredient: 1 to 20 %, preferably 5 to 10 %

Surface-active agent: 5 to 30 %, preferably 10 to 20 %
Liquid carrier: 15 to 94 %, preferably 70 to 85 %

Dusts:

Active ingredient: 0.1 to 10 %, preferably 0.1 to 1 %
Solid carrier: 99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

Active ingredient: 5 to 75 %, preferably 10 to 50 %
Water: 94 to 24 %, preferably 88 to 30 %
Surface-active agent: 1 to 40 %, preferably 2 to 30 %

Wettable powders:

Active ingredient: 0.5 to 90 %, preferably 1 to 80 %
Surface-active agent: 0.5 to 20 %, preferably 1 to 15 %
Solid carrier: 5 to 95 %, preferably 15 to 90 %

Granules:

Active ingredient: 0.5 to 30 %, preferably 3 to 15 %
Solid carrier: 99.5 to 70 %, preferably 97 to 85 %

As a rule, the active substances of the formula I are successfully employed at application rates from 0.001 to 10 kg/ha, in particular 0.005 to 2 kg/ha. The dosage rate which is required for the desired action can be determined by tests. It depends on the nature of the action, the development stage of the crop plant and the weed, as well as on the application (location, time, method) and, due to these parameters, can vary within wide limits.

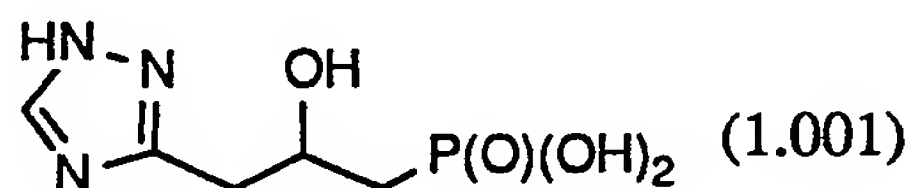
Controlled release of active substance

The dissolved active substance is applied to mineral granule carriers or polymerised granules (urea/formaldehyde) and allowed to dry. If desired, a coating can be applied (coated granules), which permits slow release of the active substance over a certain period.

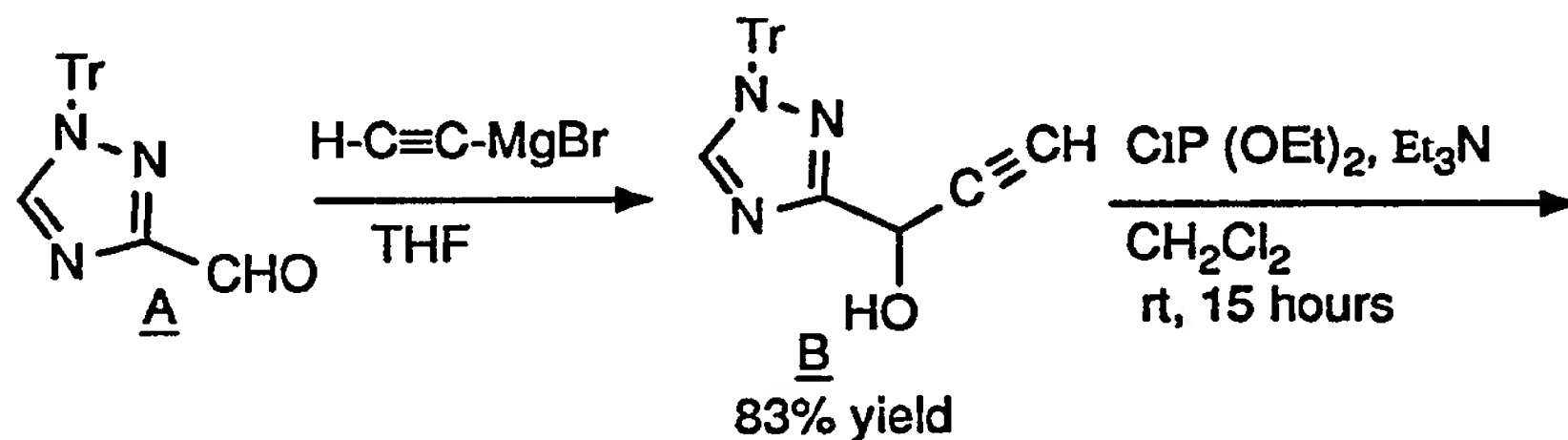
The following examples are intended to illustrate the invention in greater detail ("Tr" is the triphenylmethyl group).

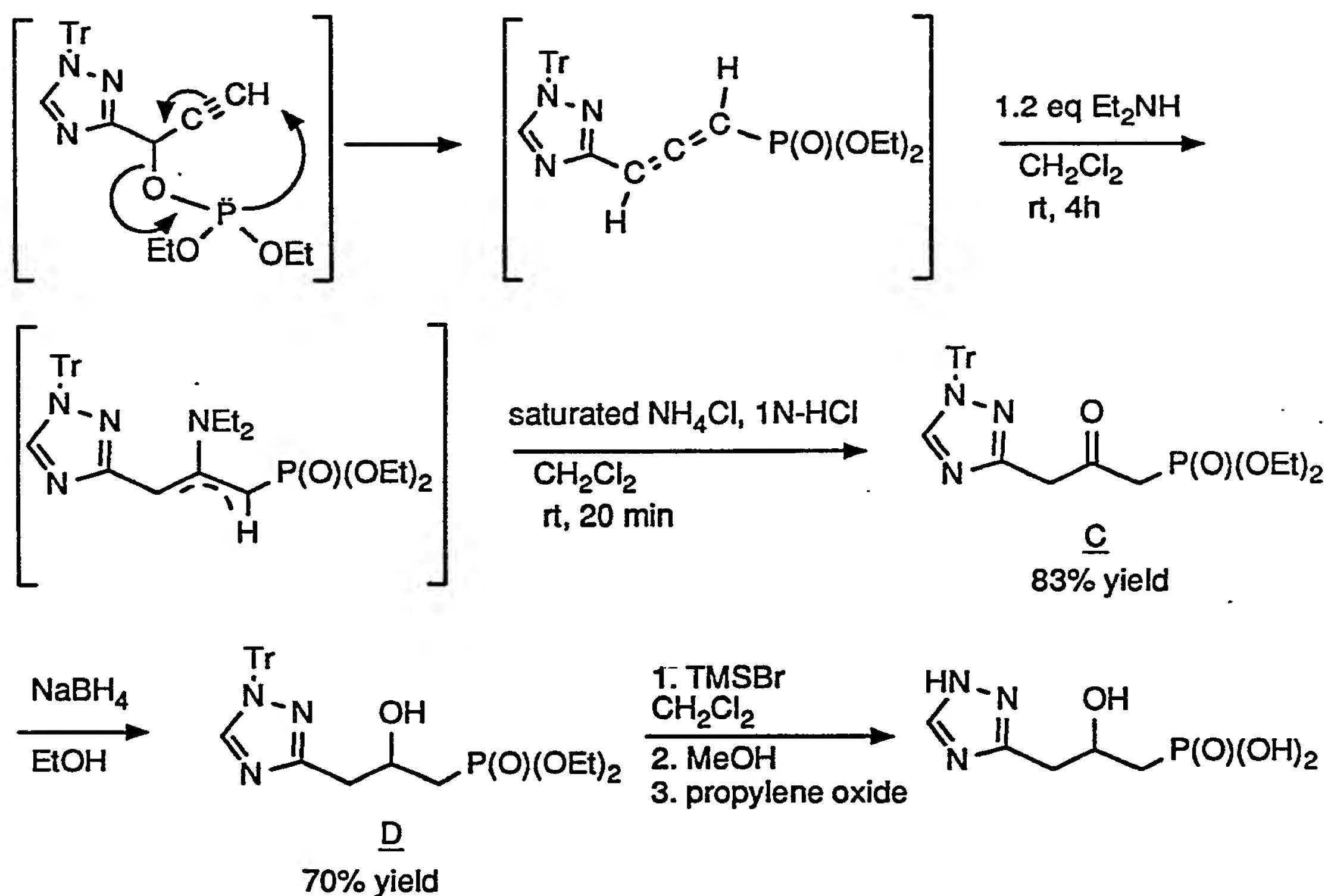
A. Preparation of compounds of formula I

Preparation of compound 1.001:

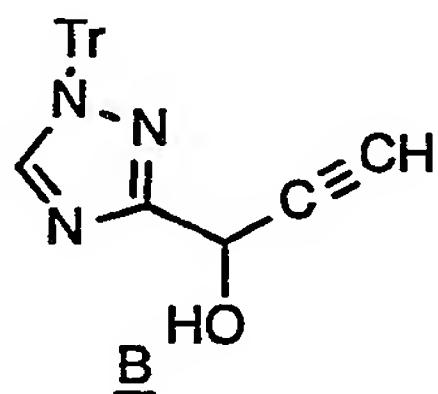


Reaction scheme:





Alcohol B

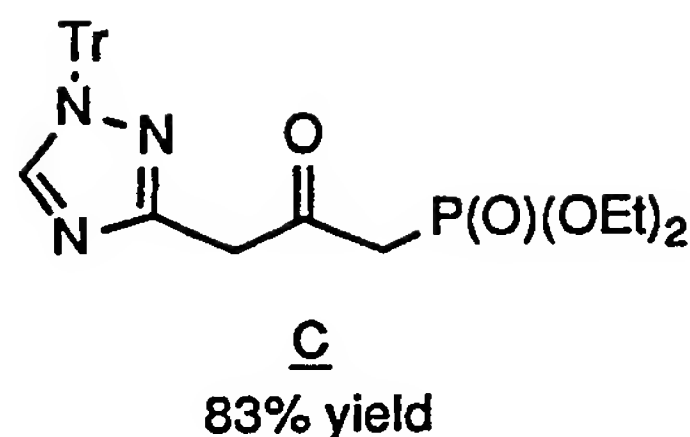


To a solution of aldehyde **A** (16.24 g, 47.8 mmol) in 300 mL of THF was added ethynyl magnesium bromide (50.0 mmol, 0.5 M in THF) at -10°C in 20 min. After stirring for 20 min, the mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl , extracted with ethyl acetate, concentrated, and triturated with ether to give 11.21 g of **B**. The mother liquor was concentrated and purified by silica gel chromatography (hexane:ethyl acetate = 1:1) to give additional 3.21 g of **B** (total yield 83 %).

mp $138-140^\circ\text{C}$

^1H NMR (90 MHz, CDCl_3) δ 7.97 (s, 1), 6.95-7.45 (m, 15), 5.61 (d, 1, $J = 2.2$), 2.55 (d, 1, $J = 2.2$). (-OH was invisible)

Ketone C

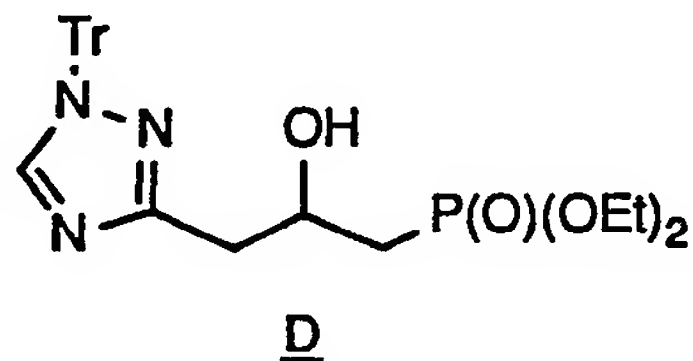


To a solution of alcohol B (8.80 g, 24.1 mmol) in 150 ml of CH_2Cl_2 , was added diethylchlorophosphite (4.20 ml, 28.9 mmol) and triethylamine (4.03 ml, 28.9 mmol) at -78°C . The mixture was stirred for 20 min at -78°C , allowed to warm to room temperature, and stirred for 15 h. Diethylamine (2.99 ml, 28.9 mmol) was added and stirred for 4 h. After addition of 50 ml of saturated aqueous NH_4Cl , 30 ml of 1N HCl was added and the mixture was stirred well for 20 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed with saturated NaHCO_3 and brine, dried over MgSO_4 . Concentration and chromatography on silica gel (ethyl acetate : methanol = 49:1) gave 9.98 g (83 % yield) of ketone C.

mp $92-95^\circ\text{C}$

^1H NMR (90 MHz, CDCl_3) δ 7.94 (s, 1), 7.22 (m, 15), 4.13 (quintet, 4, $J = 7.1$), 4.07 (s, 2), 3.20 (d, 2, $J = 22.5$), 1.30 (t, 6, $J = 7.1$).

Alcohol D

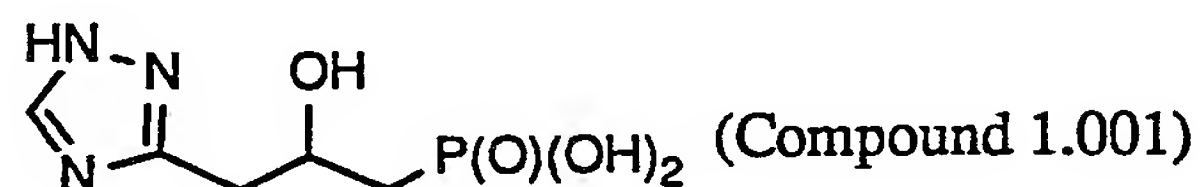


To a solution of ketone C (4.00 g, 7.94 mmol) in 15ml of ethanol was added NaBH_4 (254 mg, 6.71 mmol) and the mixture was stirred at room temperature for 2 h under nitrogen. After addition of saturated aqueous NH_4Cl , the mixture was extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 and concentrated. The desired product was crystallized by addition of hexane to the residue. The crystalline solid was collected

and dried to give 2.80 g (70% yield) of alcohol D.

mp 123-124°C

¹H NMR (90 MHz, CDCl₃) δ 7.90 (s,1), 7.25 (m,15), 4.40 (m,1), 4.08 (quintet, 4, J = 7.3), 3.04 (d, 2, J = 6.6), 2.02 (dd, 2, J = 6.6, 18.1), 1.29 (t, 6, J = 7.1).



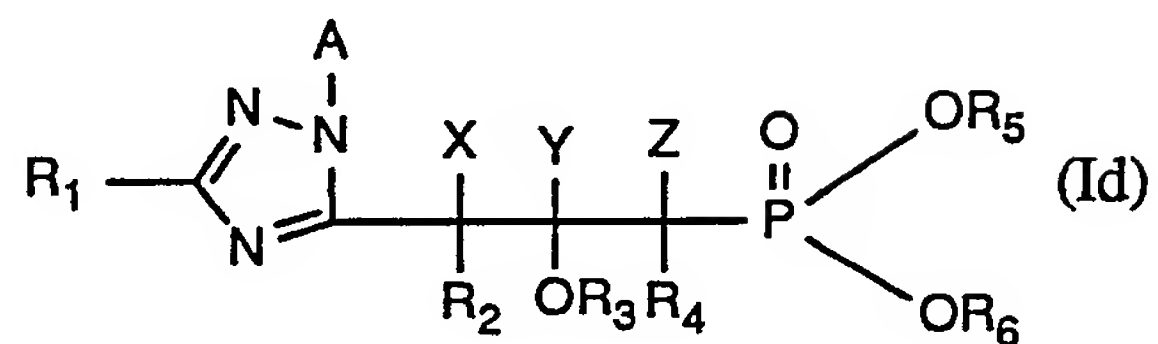
To a solution of alcohol D (0.314 g, 0.62 mmol) in 2 ml of CH₂Cl₂, trimethylsilylbromide (0.40 ml, 3.03 mmol) was added at room temperature and the mixture was stirred overnight. Methanol (0.4 ml) was added and stirred for 1 h, then propylene oxide (0.4 ml) was added dropwise to precipitate the desired product. After stirring for 1 h at room temperature, ether was added to complete precipitation. The precipitates were collected on a glass filter, washed with ether, and dried in vacuo to give 139 mg (quant.) of Compound 1.001 as very hygroscopic powder.

mp 70-90°C (hygroscopic)

¹H NMR (90 MHz, D₂O) δ 8.94 (s, 1), 4.40 (m, 1), 3.05-3.62 (m, 2), 2.03 (dd, 2, J = 17.9, 6.7).

Compounds of the formula I which are listed in Table 1 are prepared analogously to the above mentioned Examples or reaction schemes:

Table 1: Compounds of the formula Id:



Comp. No.	A	R ₁	R ₃	R ₂	R ₄	X	Y	Z	R ₅	R ₆
1.001	H	H	H	H	H	H	H	H	H	H
1.002	CH ₃	H	H	H	H	H	H	H	H	H
1.003	H	CH ₃	H	H	H	H	H	H	H	H
1.004	H	H	H	H	H	H	H	H	C ₂ H ₅	C ₂ H ₅
1.005	H	H		H	H	H	H	H	H	H
1.006	H	H		H	H	H	H	H	H	H
1.007	H	H		H	H	H	H	H	H	H
1.008	H	H		H	H	H	H	H	H	H
1.009	H	H	H	H	H	CH ₃	H	H	H	H
1.010	H	H	H	H	H	H	H	CH ₃	H	H
1.011	H	H	H	H	H	H	CH ₃	H	H	H
1.012	H	H	H	H	H	H	C ₂ H ₅	H	H	H
1.013	H	H		H	H	H	CH ₃	H	H	H
1.014	CH ₃	H	H	H	H	H	CH ₃	H	H	H
1.015	H	H	H	H	H	-(CH ₂) ₄	H	H	H	H
1.016	H	H	H	H	H	H	-(CH ₂) ₄	H	H	H
1.017	H	H	H	-(CH ₂) ₃ -	H	H	H	H	H	H

Formulation examples for active ingredients of the formula I

(% = per cent by weight)

1. Wettable powder

	a)	b)	c)
Active ingredient according to Table 1 and comp. 2.001-2.006	20 %	50 %	0.5 %
Sodium lignin sulfonate	5 %	5 %	5
Sodium lauryl sulfate	3 %	-	- %
Sodium diisobutyl naphthalenesulfonate		-	6 % 6 %
Octylphenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	2
Highly disperse silicic acid	5 %	27 %	27 %
Kaolin	67 %	- %	-
Sodium chloride	-	-	59.5 %

The active ingredient is mixed thoroughly with the additives and the mixture is ground thoroughly in a suitable mill. Wettable powders which can be diluted with water to give suspensions of any desired concentration are obtained.

2. Emulsion concentrates

	a)	b)
Active ingredient according to Table 1 and comp. 2.001-2.006	10 %	1 %
Calcium dodecylbenzenesulfonate	3 %	3 %
Octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %	3 %
Castor oil polyethylene glycol ether (36 mol of ethylene oxide)	4 %	4
Cyclohexanone	30	10 %
Xylene mixture	50 %	79 %

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

3. Dusts

	a)	b)
Active ingredient according to		

Table 1 and comp. 2.001-2.006	0.1 %	1 %
Talc	99.9 %	-
Kaolin	-	99 %

Ready-to-use dusts are obtained by intimate mixing of the carriers with the active ingredient.

<u>4. Extruded granules</u>	a)	b)
Active ingredient according to		
Table 1 and comp. 2.001-2.006	10 %	1 %
Sodium ligninsulfonate	2 %	2 %
Carboxymethylcellulose	1 %	1 %
Kaolin	87 %	96 %

The active ingredient is mixed with the additives and the mixture is ground and moistened with water. This mixture is extruded and the extrudate is then dried in a stream of air.

<u>5. Coated granules</u>	
Active ingredient according to	
Table 1 and comp. 2.001-2.006	3 %
Polyethylene glycol (molecular weight 200)	3 %
Kaolin	94 %

The finely ground active ingredient is applied uniformly to the kaolin, which has been moistened with polyethylene glycol, in a mixer. Dust-free coated granules are obtained in this manner.

<u>6. Suspension concentrate</u>	a)	b)
active ingredient according to		
Table 1 and comp. 2.001-2.006	5 %	40 %
Ethylene glycol	10 %	10 %
Nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	1 %	6 %
Sodium ligninsulfonate	5 %	10 %
Carboxymethylcellulose	1 %	1 %
37% aqueous formaldehyde solution	0.2 %	0.2 %

Silicone oil in the form of a

75% aqueous emulsion

0.8 % 0.8 %

Water

77 % 32 %

The finely ground active ingredient is intimately mixed with the additives. A suspension concentrate is thus obtained, from which suspensions of any desired concentration can be prepared by dilution with water.

7. Salt solution

Active ingredient according to

Table 1 and comp. 2.001-2.006

5 %

Isopropylamine

1 %

Octylphenol polyethylene glycol

ether (78 mol of ethylene oxide)

91 %

The compounds of the formula I are employed as such or preferably as compositions together with the auxiliaries customary in formulation technology, and they are therefore processed in a known manner to give, for example, emulsion concentrates, directly sprayable or dilutable solutions, dilute emulsions, sprayable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

Biological Examples

Example 1: Post-emergence herbicidal action (contact herbicide)

The test plants are seeded out in plastic pots containing standard soil and raised in the greenhouse at 18°C (night) and 24°C (day). Appr. 10 to 20 days after seeding (depending of individual growth-rate), foliar treatment takes place with an aqueous suspension of compound No. 1.001. The rate corresponds to 2000g a.i./ha. Appr. 2 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symptoms:

1: plants have not emerged or are totally withered

2-3: very pronounced action

4-6: medium action

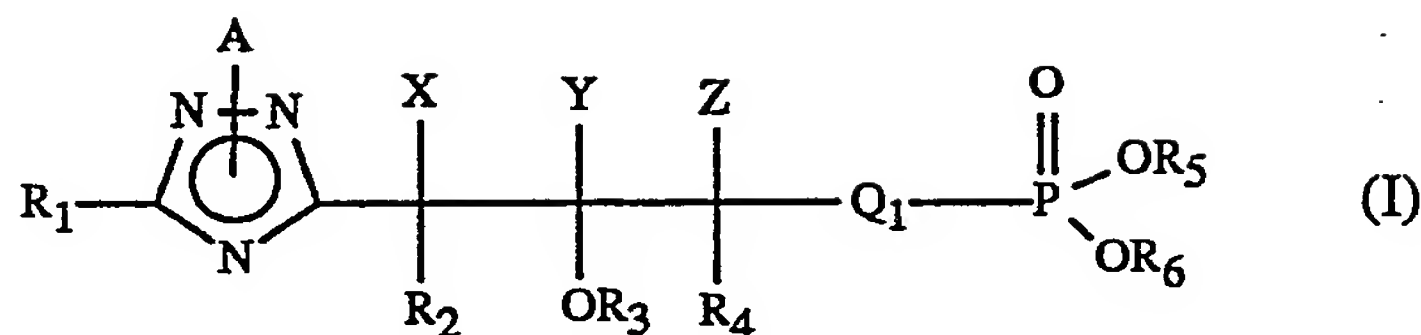
7-8: weak action

9: no action (as untreated controls).

In this test, the compound 1.001 given in Table 1 shows very pronounced herbicidal action (rating "3") against the weeds "Stellaria" and "Sinapis" and medium action (rating "4" against the weed "Setaria".

What is claimed is:

1. A triazole of the formula I



in which

A is hydrogen, C₁-C₄-alkyl, triphenylmethyl, benzyl, a group $-\text{CH}_2-\text{N} \begin{array}{c} \bigcirc \\ (\text{CH}_2)_t \end{array}$ or

SO₂N(CH₃)₂;

t is 4 or 5;

R₁ is hydrogen or C₁-C₄-alkyl;

X is hydrogen or C₁-C₄-alkyl;

Y is hydrogen or C₁-C₄-alkyl or together with X a $-\text{CH}_2-(\text{CH}_2)_p-\text{CH}_2-$ group or together with Z a $-\text{CH}_2-(\text{CH}_2)_q-\text{CH}_2-$ group;

Z is hydrogen or C₁-C₄-alkyl;

R₂ is hydrogen or C₁-C₄-alkyl;

R₃ is hydrogen, a group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Q}-\text{R}_7 \end{array}$ or a group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{R}_8 \end{array}$;

R₄ is hydrogen or C₁-C₄-alkyl, or together with R₂ a $-\text{CH}_2-(\text{CH}_2)_r-\text{CH}_2-$ group;

R₅ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R₆ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

Q is oxygen or sulfur;

Q₁ is $-(\text{CH}_2)_u-$ or $-(\text{CH}_2)_u-\text{O}-$;

R₇ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl,

C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, halomethyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl;

R₈ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, halomethyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

p is 1 or 2;

q is 1 or 2;

r is 0 or 1;

m is 0, 1 or 2;

n is 0, 1 or 2; and

u is 0 or 1.

2. A compound according to claim 1, in which

A is hydrogen, R₅ is hydrogen, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and R₆ is hydrogen, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

3. A compound of the formula I according to claim 2, in which R₁ is hydrogen.

4. A compound of the formula I according to claim 1, in which

R₁ is hydrogen; A is C₁-C₄-alkyl;

R₅ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R₆ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

5. A compound of the formula I according to claim 2, in which R₃ is hydrogen.

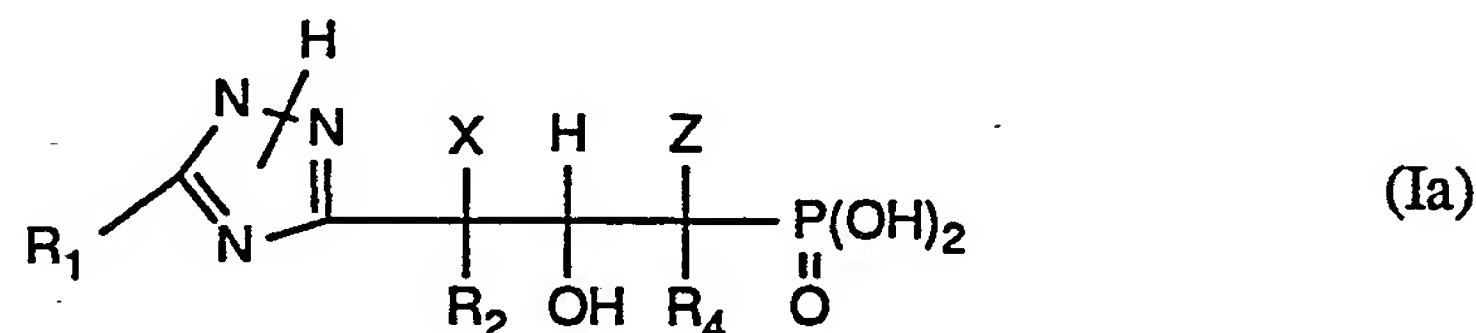
6. A compound of the formula I according to claim 1, in which R, A, R₂, R₃, R₄, R₅, R₆, X and Z each is hydrogen.

7. A compound of the formula I according to claim 1, in which

Q_1 is $-(CH_2)_u$, wherein u is 0.

8. A process for the preparation of compounds of the formula I according to claim 1, which comprises

a) for the preparation of compounds of the formula Ia

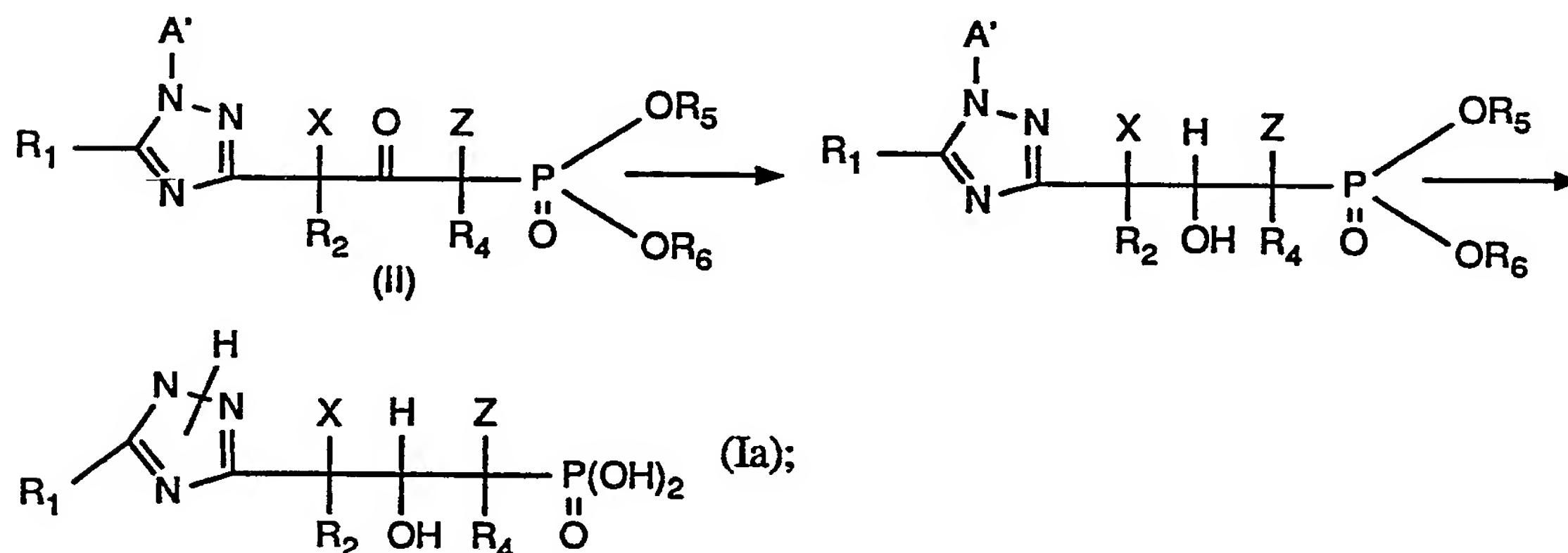


in which R_1 , R_2 , R_4 , X and Z have the meanings given in formula I in claim 1, reduction of β -ketophosphonates of the formula II, in which R_1 , R_2 , R_4 , R_5 , R_6 , X and Z have the meanings given in formula I in claim 1 and A' is triphenylmethyl, benzyl, a group

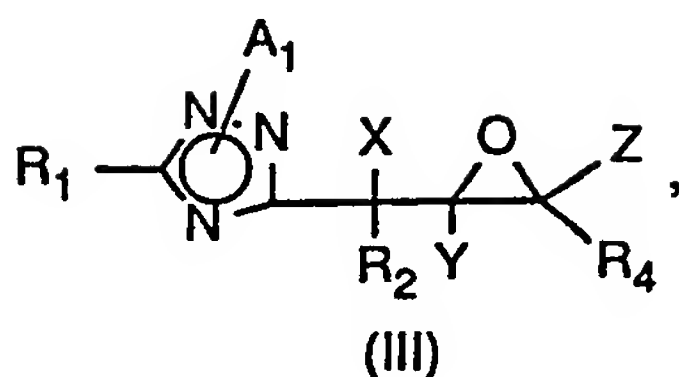
$-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl, followed by hydrolysis of

the phosphonate with an acid or a halosilane, or hydrogenolysis and cleavage of the

protecting group A' which is triphenylmethyl, benzyl, a group $-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl:



b) for the preparation of compounds of formula I, wherein R_3 is hydrogen, ring-opening of epoxides of formula III



wherein

R_1 , R_2 , R_4 , X and Z have the meanings given in formula I in claim 1, and A_1 is

C_1 - C_4 -alkyl, triphenylmethyl, benzyl, a group $-CH_2-N \bigcirc (CH_2)_t$, wherein t is 4 or 5, or

dimethylsulphamoyl, by dialkyl phosphites or dialkyl(trialkylsilyl)phosphites catalyzed by Lewis acids or a base and optionally cleaving the protecting group A_1 ;

c) for the preparation of compounds of formula I, wherein R_3 is a group $\begin{array}{c} O \\ || \\ -C-Q-R_7 \end{array}$,

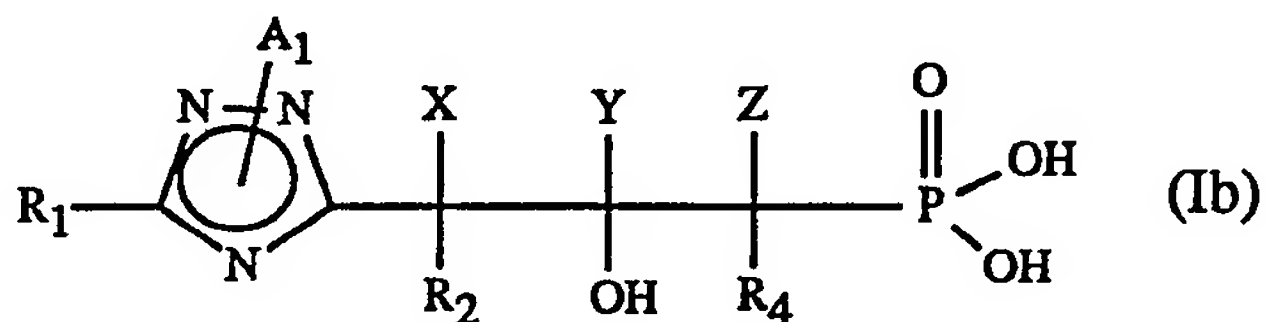
reacting a compound of formula I, wherein R_3 is hydrogen and A is A_1 mentioned above, or its sodium salt with $R_7-\begin{array}{c} O \\ || \\ QC-Halogen \end{array}$, wherein R_7 has the meaning given in formula I

in claim 1, and optionally cleaving the protecting group A_1 ;

d) for the preparation of compounds of formula I, wherein R_3 is a group $\begin{array}{c} CR_8 \\ || \\ O \end{array}$, reacting a

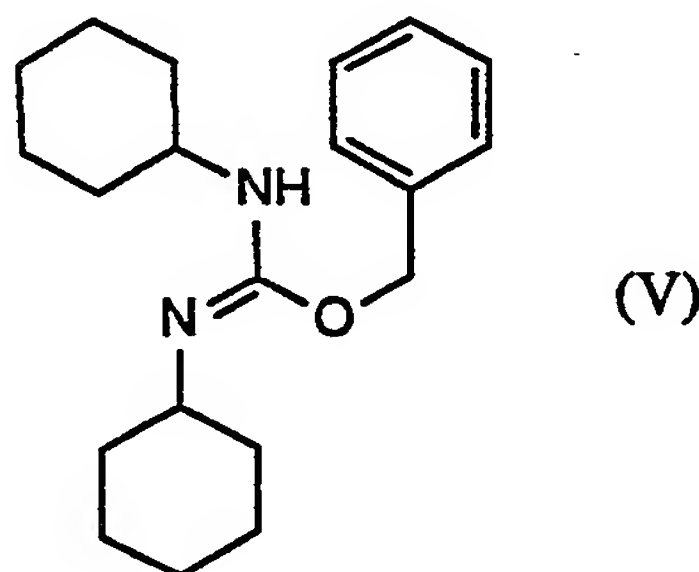
compound of formula I, wherein R_3 is hydrogen and A is A_1 mentioned above, with acid halides or anhydrides and optionally cleaving the protecting group A_1 ;

e) for the preparation of compounds of formula I, wherein R_3 is hydrogen and R_5 and R_6 are benzyl, reacting the free phosphonic acid compound Ib



wherein R_1 , R_2 , R_4 , X, Y and Z have the meanings given under formula I in claim 1 and

A_1 is C_1 - C_4 -alkyl, triphenylmethyl, benzyl, a group $-\text{CH}_2-\text{N} \bigcirc (\text{CH}_2)_t$, wherein t is 4 or 5, or dimethylsulphamoyl; with 2 equivalents of O-benzyl-N,N'-dicyclohexylisourea of the formula



to give the compound of the formula (Ic);

and optionally cleaving the protecting group A_1 .

9. A herbicidal and plant-growth-inhibiting composition, which comprises one or more triazoles of the formula I according to claim 1.

10. A composition according to claim 9, which comprises between 0.1 % and 95 % of active substance of the formula I according to claim 1.

11. A method of controlling undesired plant growth, which comprises applying an effective amount of an active substance of the formula I according to claim 1, or a composition comprising this active substance according to claim 9, to the plants or their environment.

12. A method according to claim 11, in which an amount of active substance of between 0.005 and 2 kg is applied per hectare.

13. A method according to claim 10 for selective pre-emergence or in particular post-emergence control of weeds in crops of useful plants.

14. The use of a compound according to claim 1 or of a composition according to claim 9 for controlling undesired plant growth or for regulating plant growth.

FD 4.5/IH

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report) - 34 -

Application number
GB 9220772.9

Relevant Technical fields

(i) UK Cl (Edition K) C2P
(ii) Int Cl (Edition 5) G07F

Search Examiner

D S LUCAS

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: CAS ONLINE

Date of Search

28 OCTOBER 1992

Documents considered relevant following a search in respect of claims

1-14

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	GB 2158071 A (ICI) See Claim 1	1-14
A	GB 2114133 A (ICI) See Claim 1	1-14

Category	Identity of document and relevant passages -35-	Relevant to claim

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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